

Anions (Chloride, Fluoride, Sulfate)

Summary and descriptive statistics for anions in this report are shown in Tables 8 & 9.

Table 8. Anions Summary

BMU1: ANIONS SUMMARY ¹		CHLORIDE	FLUORIDE	SULFATE
NUMBER OF SAMPLES	TOTAL:	559	559	559
BY REGION:	BLUEGRASS (INNER & OUTER):	348	348	348
	EASTERN COAL FIELD:	133	133	133
	MISSISSIPPIAN PLATEAU:	74	74	74
	OHIO RIVER ALLUVIUM:	4	4	4
NUMBER OF DETECTIONS	TOTAL:	552	556	548
	% DETECTS (vs SAMPLES):	98.7%	99.5%	98.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	348	346	347
	EASTERN COAL FIELD:	126	132	124
	MISSISSIPPIAN PLATEAU:	74	74	73
	OHIO RIVER ALLUVIUM:	4	4	4
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	5	3	50
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	0.9%	0.5%	9.1%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	0.9%	0.5%	8.9%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	2
	EASTERN COAL FIELD:	5	3	48
	MISSISSIPPIAN PLATEAU:	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0
NUMBER OF SITES	TOTAL:	57	57	57
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33	33
	EASTERN COAL FIELD:	19	19	19
	MISSISSIPPIAN PLATEAU:	4	4	4
	OHIO RIVER ALLUVIUM:	1	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	57	57	56
	% SITES W/DETECTIONS:	100.0%	100.0%	98.2%
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33	33
	EASTERN COAL FIELD:	19	19	18
	MISSISSIPPIAN PLATEAU:	4	4	4
	OHIO RIVER ALLUVIUM:	1	1	1
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	2	1	7
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	3.5%	1.8%	12.5%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	3.5%	1.8%	12.3%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	2
	EASTERN COAL FIELD:	2	1	5
	MISSISSIPPIAN PLATEAU:	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0
CHLORIDE	MCL (mg/L)	Secondary (mg/L)		Other
FLUORIDE	-	250		-
SULFATE	4	-		-
	-	250		-
¹ Only 559 anion values out of 565 samples: 6 analyses: lab analyses did not include IC Anion Scan method.				

Table 9. Anions Descriptive Statistics

BMU1: ANIONS DESCRIPTIVE STATISTICS						
	CHLORIDE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	04/26/95	06/11/03	1770	13.2	0.584	< 1.0000
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	189	16.9	1.16	13.7
EASTERN COAL FIELD:	05/02/95	05/28/03	1770	4.82	0.584	< 1.0000
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	33.2	3.5	1.1	1.1
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	32.8	29.15	27.2	-
	FLUORIDE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	04/26/95	06/11/03	17.5	0.196	< 0.008	0.21
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	1.3	0.21	0.01	0.21
EASTERN COAL FIELD:	05/02/95	05/28/03	17.5	0.17	< 0.008	0.05
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	0.22	0.09	0.01	0.06
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.149	0.141	0.114	-
	SULFATE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	04/26/95	06/11/03	4280	43.6	0.216	< 5.0000
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	4280	38.65	1.39	34.9
EASTERN COAL FIELD:	05/02/95	05/28/03	1583	181	0.216	< 5.0000
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	108	59.15	< 5.0000	7.7
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	66	59.2	56	-

Chloride (Cl) is naturally occurring in most rocks and soils and is the primary constituent that makes water "salty". Chloride also occurs in sewage, industrial brines and in urban runoff from the application of road salt. Brine water, or "connate water", occurs in the pore spaces and fractures of rocks and is sometimes found at shallow depths, especially in eastern Kentucky. Typically, however, water gradually becomes saltier as the depth increases. Over-pumping of fresh water in some wells can induce chloride-rich brines, which occur at depth to move, or "up well," toward the discharge point. This phenomenon is known as "salt water intrusion." As nonpoint source pollutants, chlorides are also associated with crude oil and are commonly produced as a by-product when oil is pumped to the surface. For disposal, these brines are typically re-injected into very deep and already briny, formations. Further, chloride-rich brines can contaminate freshwater aquifers through improperly cased or abandoned oil production wells.

Chloride was found in 552 of 559 samples (98.7%), but median values were low, 13.1 mg/L (Tables 8 & 9). Most chloride values clustered in a narrow range (Figures 12 and 13). Variations in chloride occurrence in BMU 1 appear to be the result of underlying geology, rather than nonpoint sources. Maximum values in this study were found in two wells in the Eastern Coal Field (Figure 14): Mountain Heritage in Letcher County (1770 mg/L) and four samples around 800 mg/L were found at Rousseau School in Breathitt County. Chlorides are known to occur at shallow depths in eastern Kentucky, and although oil wells and associated brine could affect groundwater in this province, none were noted in the immediate vicinity of these two sites.

No apparent impacts on groundwater quality from chloride from nonpoint sources were indicated in this study. Median values are low, reflecting normal groundwater quality variation. Fluoride (F) commonly occurs in trace quantities in many soils and rocks, including coal. Fluorite (CaF_2) is the primary fluorine mineral. Fluoride in the form of hydrogen fluoride enters the environment through atmospheric deposition from coal-fired power plants and from some manufacturing processes, especially aluminum smelting. Because small amounts of fluoride (1 ppm) in water help prevent tooth decay, public water systems often add this to their water. Some researchers claim this practice is potentially harmful and therefore the efficacy of drinking water fluoridation is a widely debated issue. The MCL for fluoride is 4 mg/L. Exposure to excessive amounts of fluoride can result in dental and skeletal fluorosis. Dental fluorosis is characterized by brittle, mottled and discolored tooth enamel and skeleton fluorosis causes a wide range of muscle and bone problems, including osteoporosis.

Conrad and others (1999a) compiled and analyzed statewide fluoride data. They reviewed 4,848 records from 2,630 sites and found only 24 analyses from 16 sites that exceeded the MCL.

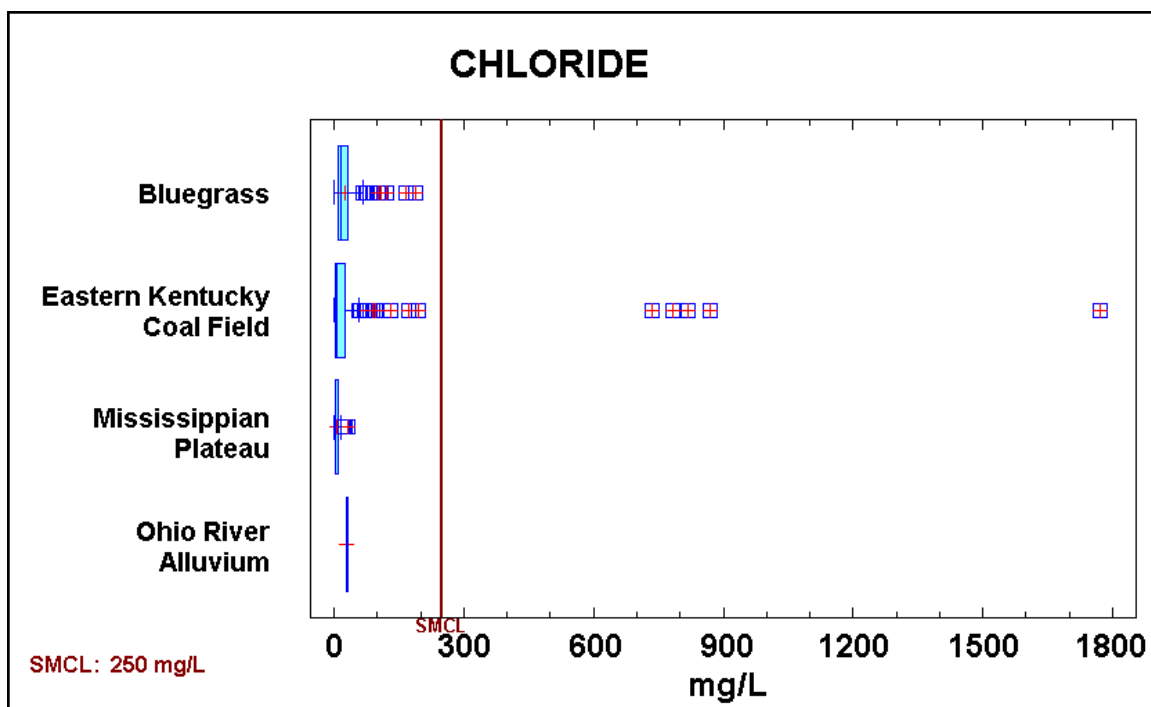


Figure 12. Boxplot of Chloride and Physiographic Regions

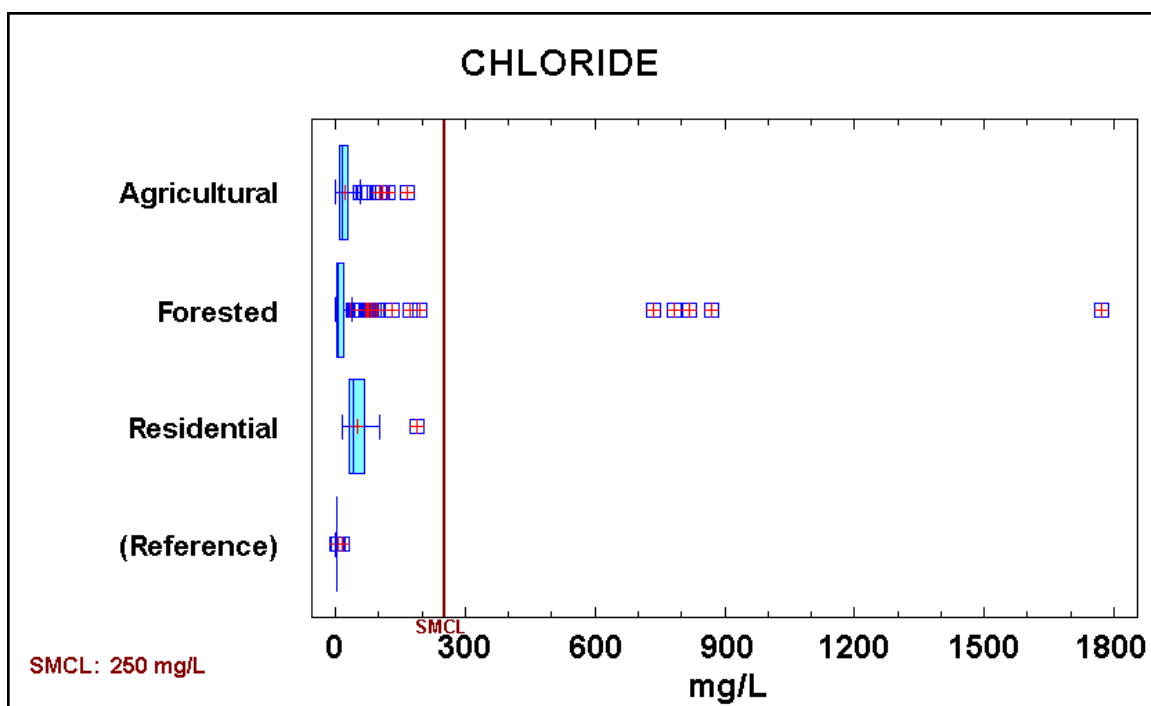


Figure 13. Boxplot of Chloride and Land Use

BMU 1

Median Chloride Data

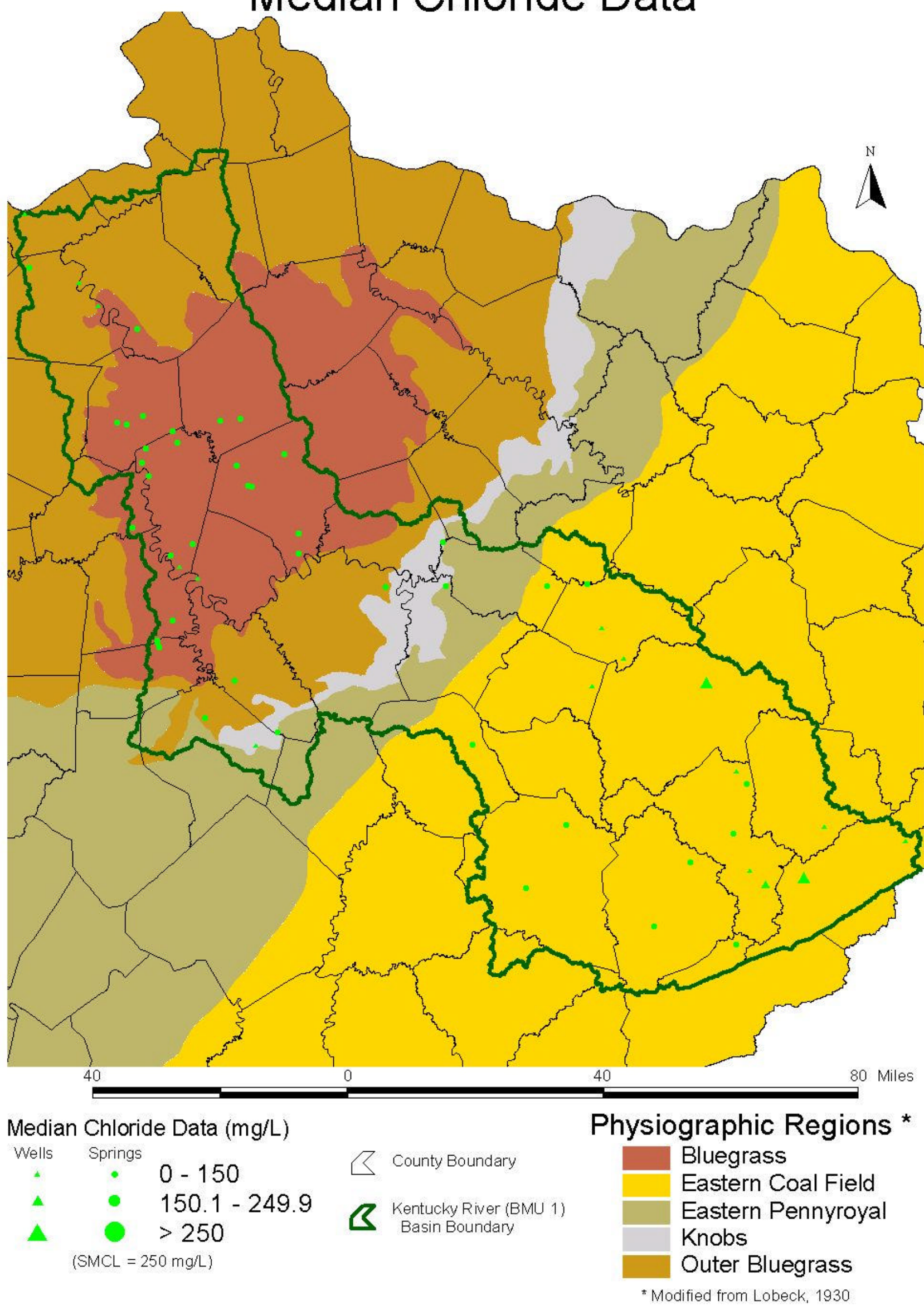


Figure 14. Chloride Map

As shown in Tables 8 & 9, fluoride was detected in 99.5% of the samples analyzed in this study (556/559), but was only found above MCL in four samples from two sites. These were Russell Cave Spring in Fayette County (64.8 mg/L) and the Viper Elementary School well in Perry County, where the highest value found was 17.5 mg/L. The one exceedance at Russell Cave is unexplained. However, the high values at Viper are the result of the removal of the raw water sampling tap and the installation of an in-line fluorinator that may have caused backflow into the well and also precluded the collection of a raw water sample. (Samples collected from the raw water tap before its removal measured less than 1.0 mg/L.)

High values shown in Figures 15 and 16 for forests and the Eastern Coal Field reflect the unexplained occurrence at Russell Cave Spring and the explained occurrence at Viper. Median values of fluoride ranged from 0.09 mg/L in the Mississippian Plateau to 0.141 in the Ohio River Alluvium, and are illustrated in Figure 17. This study suggests that fluoride is naturally-occurring in Kentucky's groundwater at low levels and no evidence was found that this parameter results from nonpoint source pollution.

Sulfate (SO_4) typically dissolves into groundwater from gypsum (hydrous calcium sulfate) and anhydrite (calcium sulfate), from the oxidation of several iron sulfides, such as pyrite (FeS) and from other sulfur compounds. In BMU 1 sulfate is common and naturally occurring, and therefore it is not a good indicator of nonpoint source pollution. Sulfate has an SMCL of 250 mg/L and amounts greater than this impart distasteful odor and taste to the water and commonly have a laxative effect.

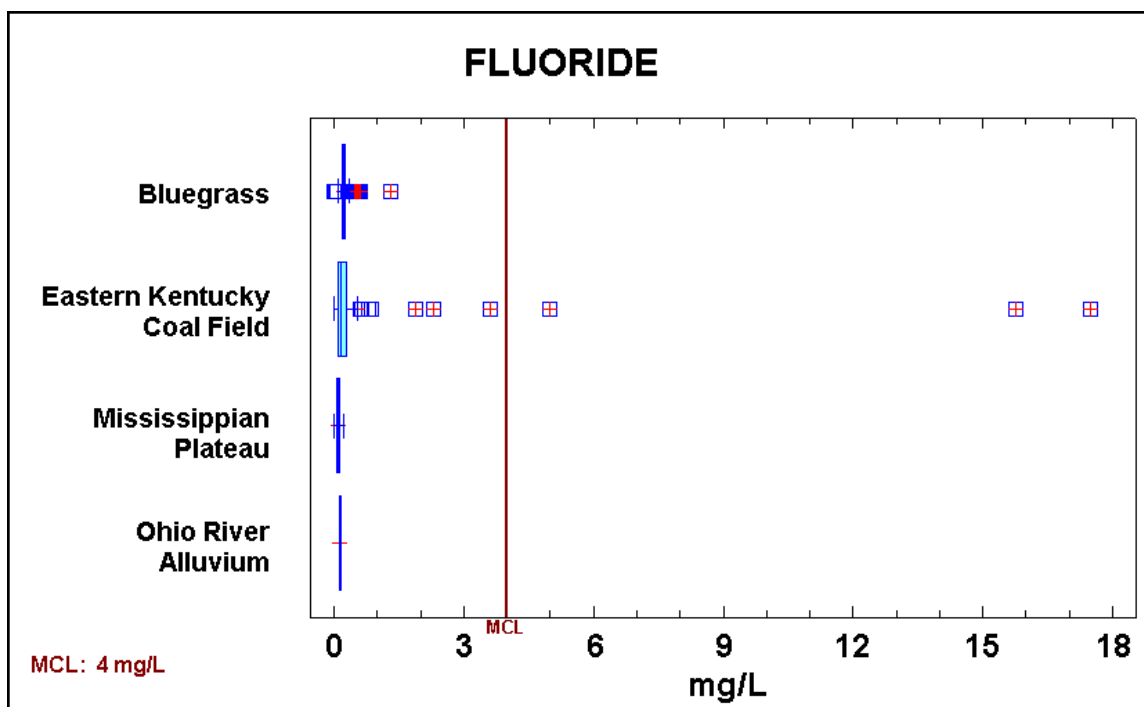


Figure 15. Boxplot of Fluoride and Physiographic Regions

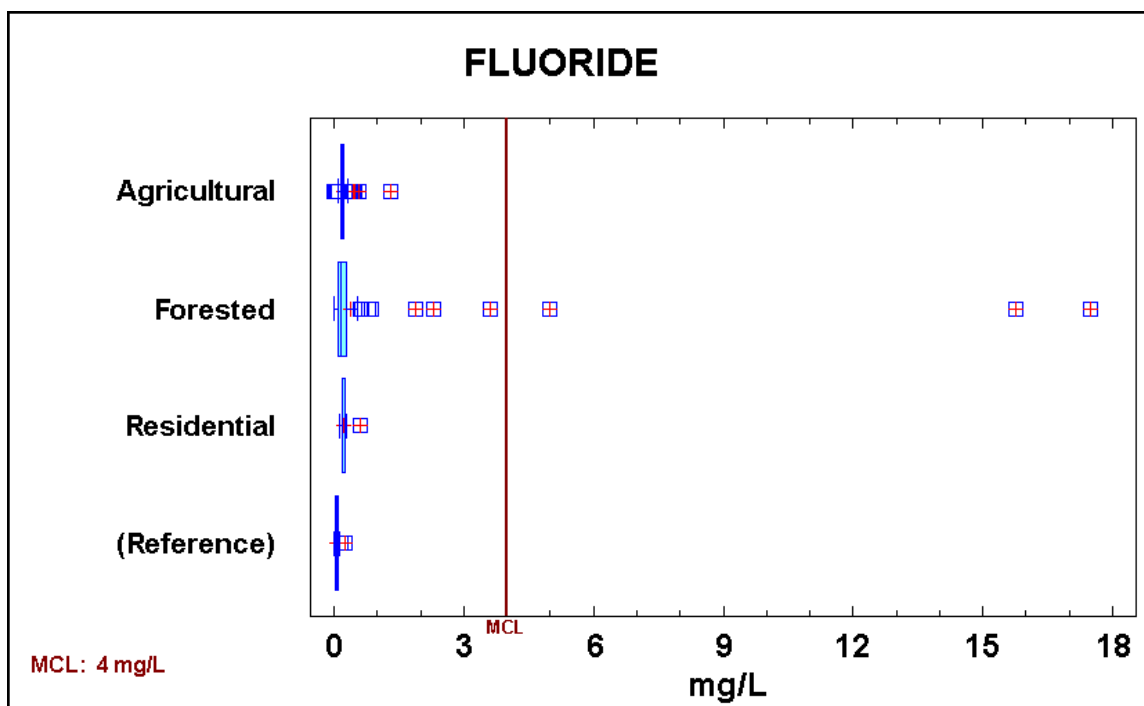


Figure 16. Boxplot of Fluoride and Land Use

BMU 1

Median Fluoride Data

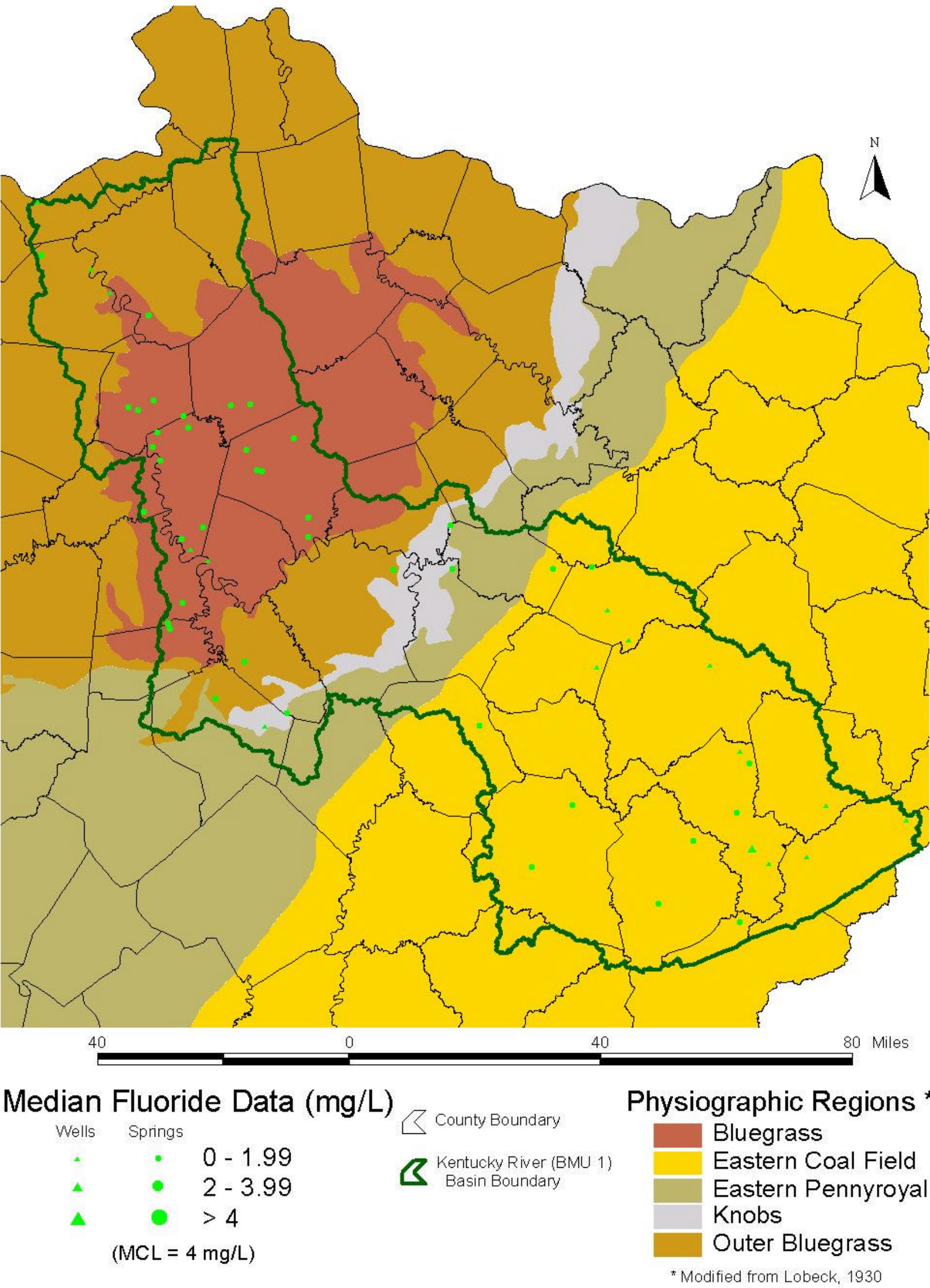


Figure 17. Fluoride Map

Sulfate was analyzed in 559 samples (Table 8) and was detected in 548 (98%). The Eastern Coal Field had the highest median value of 181 mg/L, and the Bluegrass the lowest, 38.65 mg/L (Table 9). The Mississippian Plateau and the Ohio River Alluvium had almost identical medians of 59.15 mg/L and 59.2 mg/L respectively. Boxplots (Figures 18 and 19) show that most sulfate values occur within narrow ranges whether plotted against physiographic provinces or land use, but outliers are common in the Bluegrass and the Eastern Coal Field and in agricultural and forested areas. Two springs in the Bluegrass, McCall's and Russell Cave, had single occurrences of anomalously high sulfate, which are unexplained, and two sites in the Eastern Coal Field, Dad's and Aunt Soph's springs had consistently high sulfate, which is known to occur naturally at high levels in this physiographic province. Distribution of sulfate in BMU 1 is shown in Figure 20.

The occurrence of sulfate in BMU 1 is believed to be naturally occurring and is not a nonpoint source contaminant of concern.

Metals (Arsenic, Barium, Iron, Lead, Manganese and Mercury)

For this report, groundwater data were reviewed for arsenic, barium, iron, lead, manganese and mercury. Barium, iron, and manganese were the most common metals found; lead and arsenic were much less common; and mercury was only detected in one sample. Summaries and descriptive statistics of the six metals included in this study are shown in Tables 10 and 11.

These metals were chosen because they are important contributors to ambient groundwater quality and can be introduced as pollutants from nonpoint source activities. They are common to trace constituents of soils (Logan and Miller, 2002) and sedimentary rocks, including limestone, dolostone, coal and black shales (Dever, 2000; USGS, 2002b; Tuttle and others, 2001). In water, low pH values and higher dissolved oxygen content increase the dissolution of metals. Common

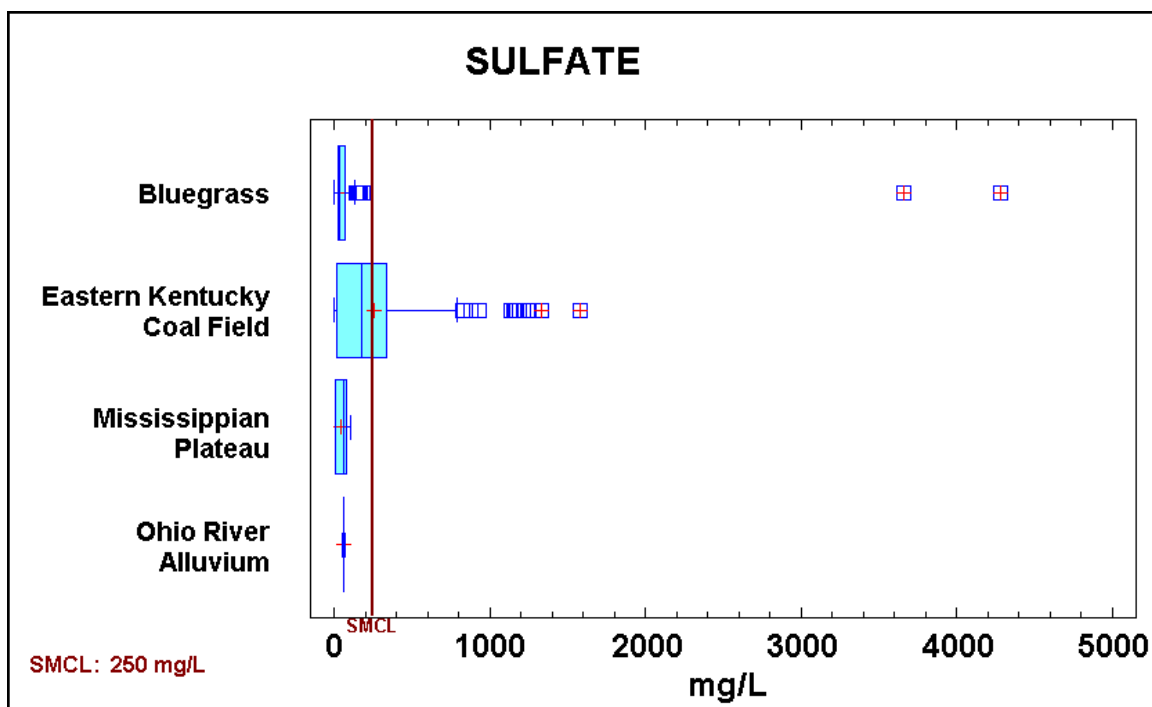


Figure 18. Boxplot of Sulfate and Physiographic Regions

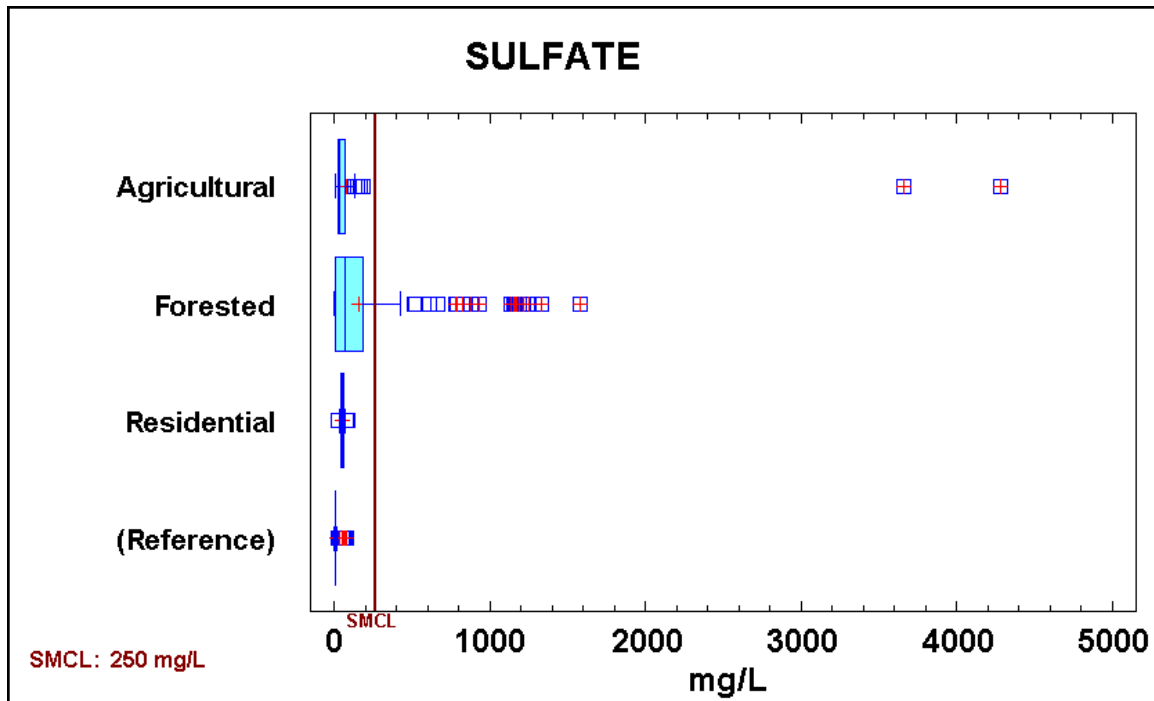


Figure 19. Boxplot of Sulfate and Land Use

BMU 1

Median Sulfate Data

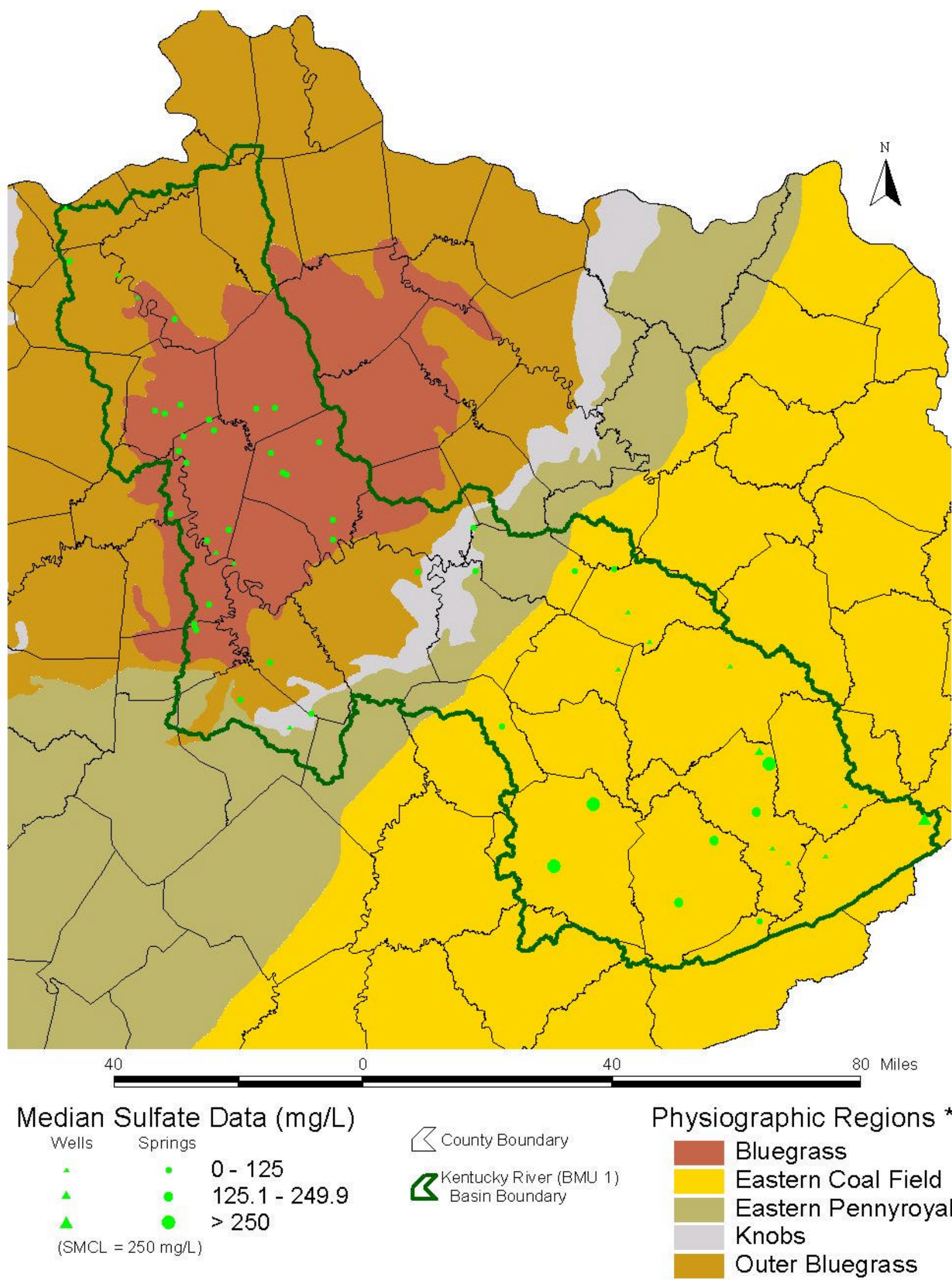


Figure 20. Sulfate Map

Table 11. Metals Descriptive Statistics

BMU1: METALS DESCRIPTIVE STATISTICS						
	ARSENIC (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	11/05/97	06/11/03	0.076	< 0.002	< 0.0005	< 0.002
BLUEGRASS (INNER & OUTER):	11/05/97	06/11/03	0.076	< 0.002	< 0.0005	< 0.002
EASTERN COAL FIELD:	03/11/98	05/28/03	0.008	< 0.002	< 0.001	< 0.002
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	< 0.002	< 0.002	< 0.001	< 0.002
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.002	< 0.002	< 0.002	< 0.002
	BARIUM (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	02/10/98	06/11/03	2.95	0.029	< 0.001	0.016
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	0.328	0.026	< 0.001	0.023
EASTERN COAL FIELD:	03/11/98	05/28/03	2.95	0.03225	0.008	0.031
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	0.063	0.03	0.019	0.038
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.116	0.108	0.1	0.108
	IRON (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	02/10/98	06/11/03	20.8	0.112	< 0.001	< 0.007
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	12.2	0.1205	< 0.001	< 0.007
EASTERN COAL FIELD:	03/11/98	05/28/03	20.8	0.127	< 0.001	< 0.007
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	0.75	0.056	< 0.005	0.02
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	1.16	0.663	0.56	-
	LEAD (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	11/05/97	06/11/03	0.042	< 0.002	< 0.001	< 0.002
BLUEGRASS (INNER & OUTER):	11/05/97	06/11/03	0.042	< 0.002	< 0.001	< 0.002
EASTERN COAL FIELD:	03/11/98	05/28/03	0.013	< 0.002	< 0.001	< 0.002
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	< 0.002	< 0.002	< 0.001	< 0.002
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.017	0.0035	< 0.002	-
	MANGANESE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	02/10/98	06/11/03	1.38	0.015	< 0.001	< 0.001
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	1.01	0.018	< 0.001	< 0.001
EASTERN COAL FIELD:	03/11/98	05/28/03	1.38	0.015	< 0.001	< 0.005
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	0.035	0.003	< 0.001	< 0.001
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.143	0.133	0.128	-
	MERCURY (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	02/10/98	06/11/03	0.000065	< 0.00005	< 0.00005	< 0.00005
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	0.000065	< 0.00005	< 0.00005	< 0.00005
EASTERN COAL FIELD:	03/11/98	05/28/03	< 0.00005	< 0.00005	< 0.00005	< 0.00005
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	< 0.00005	< 0.00005	< 0.00005	< 0.00005
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00005	< 0.00005	< 0.00005	< 0.00005

anthropogenic nonpoint sources of metals include mining, urban run-off, industrial operations, land farming of sewage and other waste and emissions from coal-fired power plants. The provenance of high concentrations of metals in groundwater is sometimes difficult to interpret and may indicate point sources, nonpoint sources, or natural sources. Comparison with reference reach springs (Table 5), as well as reviewing relevant literature, can prove useful.

A complete suite of total and dissolved metals was analyzed for each sample collected. Because MCLs are based upon total metal analysis, the results presented below are for total, rather than dissolved, concentrations. Although several other metals, such as silver, vanadium and gold were analyzed, detections of these were exceedingly rare and invariably at very low concentrations. Consequently, these results are not presented here.

Arsenic (As) is found as a trace element in coal, shale, limestone, and dolostone (USGS, 2002b; Dever, 2000). Arsenic-containing minerals, occurring as veins or disseminated in sedimentary rocks or soils derived from them, include arsenopyrite (FeAsS), pyrite and marcasite (different crystalline forms of FeS_2), and sphalerite (ZnFeS). The most prevalent use of arsenic is as a wood preservative, but other anthropogenic sources include atmospheric deposition from coal-fired power plants and metal-smelting/manufacturing processes. Historical and current agricultural use of arsenic-containing pesticides is very limited, according to Collins (Kentucky Division of Pesticides, personal communication May, 2004) with only about 250 pounds of arsenic sold in 2002 (Division of Pesticides, 2002). Another historic use of arsenic included embalming fluid, especially from about 1860 until its use was banned in 1910 (Fetter, 1992).

Arsenic occurs in organic and inorganic forms and generally the latter are more harmful to human health, where arsenic exposure has been linked to bladder and other cancers (USGS, 2000). Arsenic has an MCL of 0.010 mg/L, which was lowered by the US EPA from 0.05 mg/L in 2001. Public water utilities will be required to meet the new standard by January 2006.

Blanset and Goodmann (2002) reviewed the occurrence of arsenic in Kentucky's groundwater. In their study of 1,249 ambient groundwater samples from 240 sites, they found 10 sites with one or more samples exceeding the MCL. They suggested that the "... most prominent source of arsenic in Kentucky's aquifers results from the oxidation of arsenopyrite, incorporated in iron hydroxides." Welch and others (1999) reached a similar conclusion in their review of national data and the USGS (2002a) states that the majority of arsenic in groundwater is the "... result of minerals dissolving from weathered rocks and soils." In his review, which

included historical data of varying quality, Fisher (2002) found that for ambient groundwater about 95% of 4,402 analyses from 930 sites were less than the MCL.

For this study, arsenic was analyzed for 395 samples (Table 10) and was detected in 15 (3.8%), and the median value was 0.002 mg/L (Table 11). One site, the Glenwood Hall well in Owen County, exceeded the MCL in five samples. This well produces from alluvium adjacent to the Kentucky River, and therefore its chemistry is not typical of the carbonate aquifers underlying the Bluegrass. Arsenic, and other metals, in this well may be related to the erosion upstream on the Kentucky River of mineralized veins containing arsenic and the deposition of these metal-rich sediments in the alluvium, combined with reduced conditions in the aquifer or at the borehole.

Boxplots of arsenic compared to physiographic provinces and land use are shown in Figures 21 and 22, and map distribution in Figure 23. Arsenic has a narrow range of occurrence at low values, but outliers are common. Most of the high outliers in the forest and Bluegrass are the result of detections at the Glenwood Hall well.

In summary, the occurrence of arsenic in BMU 1 groundwater is from natural processes and this metal is not a nonpoint source pollutant of concern at this time.

Barium (Ba) occurs most commonly as the mineral barite (BaSO_4) but also as witherite (BaCO_3). Barium occurs in the shales and coals of the Eastern Coal Field where Wunsch (1991) determined that sulphur-reducing bacteria in Eastern Coal Field aquifers affects the chemical equilibrium of groundwater “. . . thus allowing for greater concentrations of barium to exist in solution.” Barium is also found as mineralized veins within the limestones and shales of the Inner Bluegrass of central Kentucky. Barium is used in a variety of products including drilling mud, glass and paint. The MCL for barium is 2.0 mg/L and exposure to high levels of barium has been associated with cardiovascular problems such as high blood pressure.

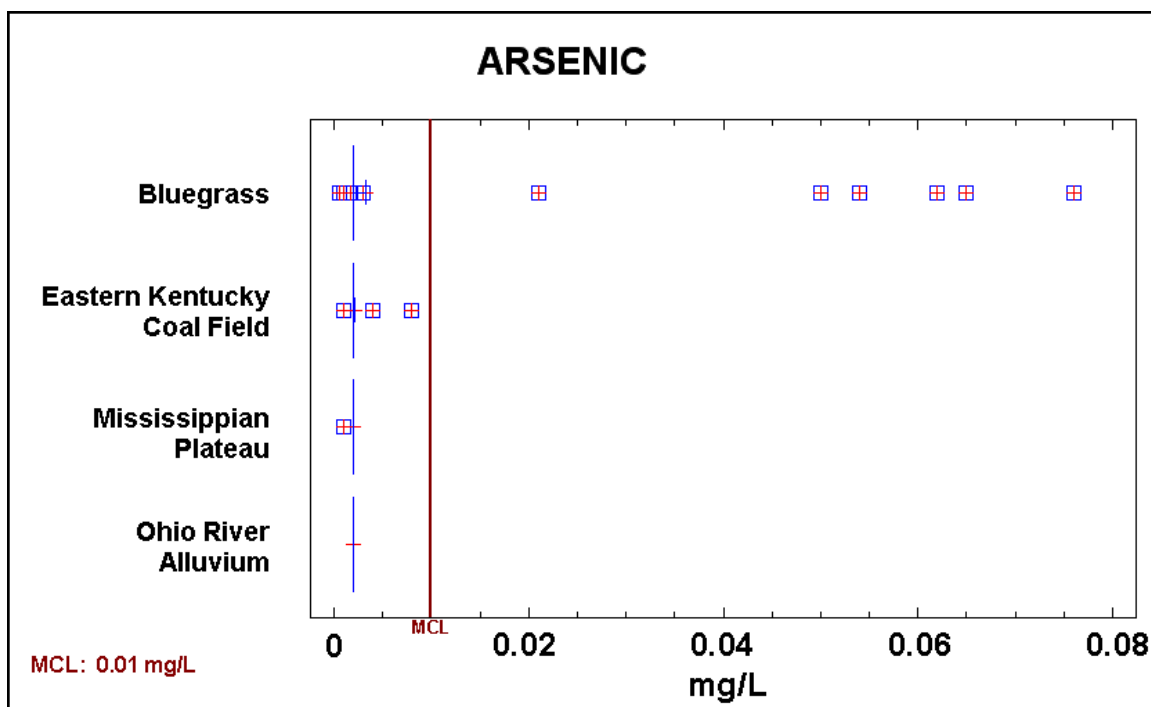


Figure 21. Boxplot of Arsenic and Physiographic Regions

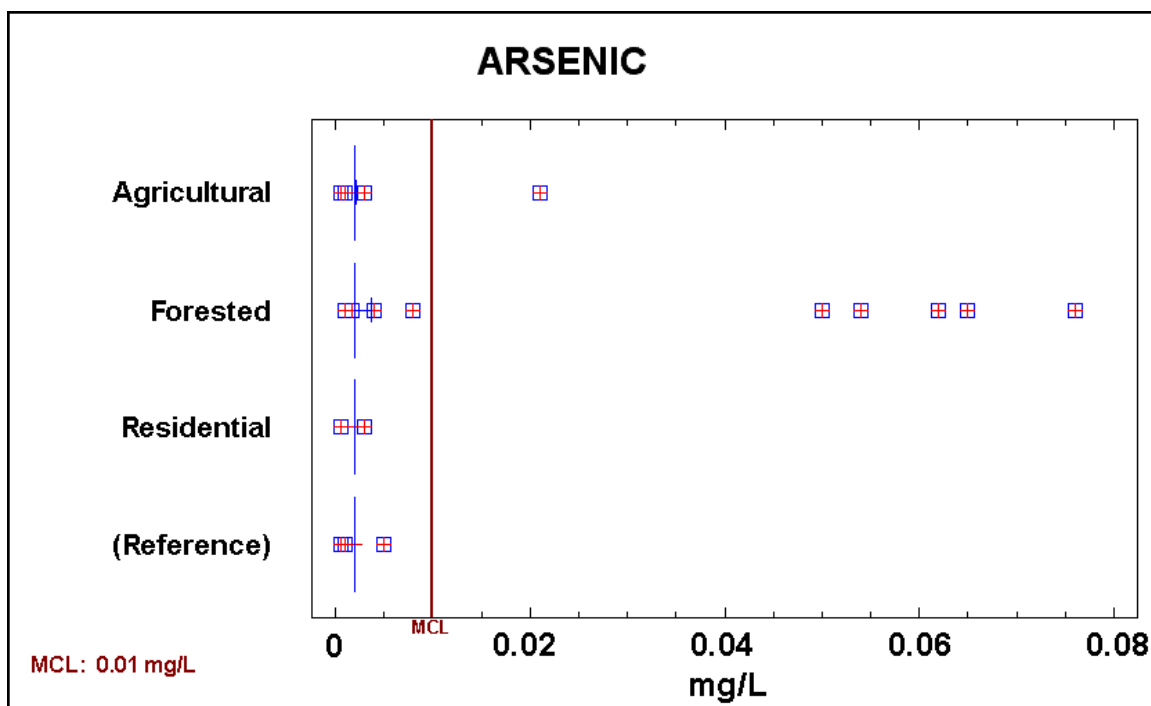


Figure 22. Boxplot of Arsenic and Land Use

BMU 1 Median Arsenic Data

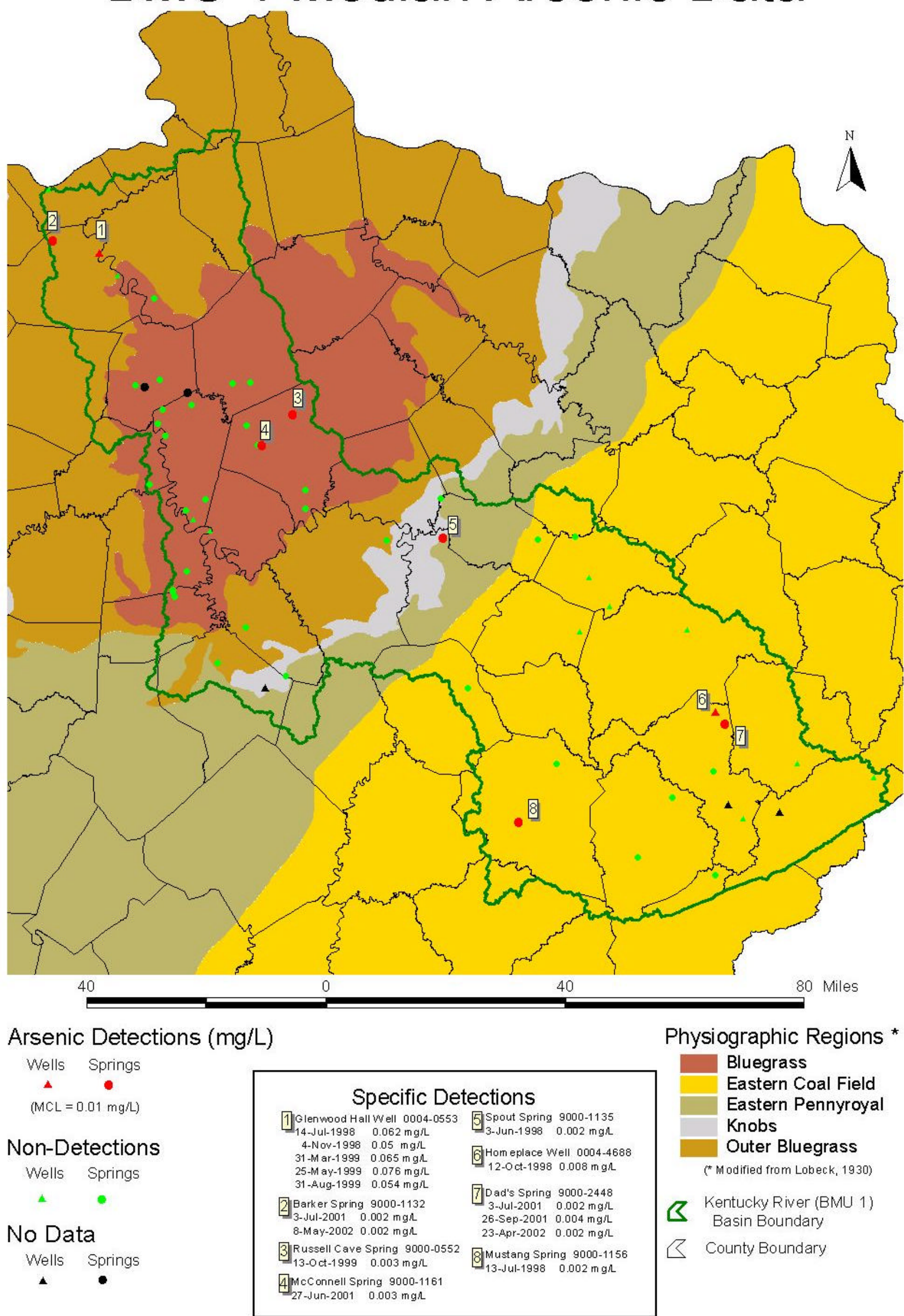


Figure 23. Arsenic Map